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(71) Applicant: AGFA-GEVAERT naamloze vennootschap
Septestraat 27
B-2510 Mortsel(BE)

(72) Inventor: Leenders, Luc Herwig
Lichtaartseweg 182
B-2410 Herentals(BE)
Inventor: De Schryver, Frans Carl
Minnezang 9
B-3202 Linden(BE)
Inventor: Quanten, Erwin
Dellestraat 24
B-3020 Herent(BE)

(54) A process for the production of a photothermographic material.

(57) A process for the production of a photothermographic material including the steps:

1) producing inverted micelles having a polar core by mixing a surfactant in an non polar liquid medium in the presence water being used in a minor amount with respect to the non polar liquid,

2) allowing to react halide ions with silver ions in the polar core of said micelles obtaining thereby inverted micelles having in their core minute amounts of silver halide,

3) optionally introducing also in the core of said micelles an aqueous liquid medium comprising a hydrophilic colloid, e.g. gelatin,

4) forming a film forming photosensitive coating composition by mixing said micelles in said non polar liquid medium with a film forming polymeric organic binding agent that is soluble in said liquid medium, said liquid medium optionally also comprising a dissolved or dispersed developing agent for photo-exposed silver halide, and

5) coating said compostion onto a support and allowing the non polar liquid to evaporate leaving a solid photsenstive layer on said support.

EP 0 227 141 A1

A PROCESS FOR THE PRODUCTION OF A PHOTOTHERMOGRAPHIC MATERIAL

The present invention relates to a photothermographic recording material and process for the production thereof.

A photothermographic recording material is a light-sensitive material that can be processed by application of heat to form a visible image after its image-wise exposure to light.

Conventional silver halide recording materials with all their enormous advantages have a severe limitation in that they have to be processed in wet state using mostly several processing liquids. This is a drawback that has given the impuls to a search for silver halide systems that retain the basic advantageous properties inherent to the use of silver halide but offer access to an image in a dry process.

A dry imaging process based on the use of silver halide as photosensitive substance is described e.g. in GB-P 1,110,046 and operates with an imaging layer having the following two main components :

(a) a comparatively small amount of silver halide,

(b) a major amount of non-light-sensitive image forming material, more particularly a silver soap, e.g. silver behenate plus a reducing agent.

The components (a) and (b) must be in catalytic proximity which means that the photolytic silver from the silver halide must be capable to catalyse the image-forming redox-reaction between the silver soap and the reducing agent while heating the recording layer for a few seconds to approximately 100°C so that hereby a silver image develops.

A good light-sensitivity is attained when the necessary silver halide is formed in situ at the surface of the non-light-sensitive silver salt by reaction with a compound yielding halide ions, e.g. as described in US-P 3,457,075 and 3,770,448. A material obtained that way has a sensitivity in the short wave region of the visible spectrum in accordance with the inherent sensitivity of the silver halides formed and can be spectrally sensitized to light of longer wavelengths by the addition of spectral sensitizing dyes.

According to one embodiment described in US-P 3,457,075 the formation in situ of silver halide proceeds with hydrogen bromide as a source of halide ions in equal volumes of alcohol and water wherein a silver soap is dispersed. The dispersion is mixed thoroughly by stirring whereby the silver halide is formed in situ, i.e. in reactive association with the other components needed for the photothermographic image formation.

According to another embodiment described in said last mentioned US-P a first coating is made of silver soap, e.g. silver stearate, in a binder such as polyvinyl butyral from a mixture of non polar solvent such as toluene and a polar solvent such as acetone and a second coating is applied thereon containing ammonium bromide, hydroquinone, spectral sensitizing agent and polyvinyl pyrrolidone from acetone. The ammonium bromide amounts to approximately four molar percent of silver stearate.

According to an embodiment described in US-P 3,770,448 the silver halide is produced in situ in the recording layer by treating the non-lightsensitive silver salts at their surface with vapours of hydrohalic acids, e.g. hydrogen chloride in the vapour phase.

As is generally known chemical reactions wherein ionic substances take part, proceed at higher rate and yield in media including a polar solvent than in media having a non polar character since a polar solvent gives rise to the dissociation of the ionic substances in their reactive ions.

In J. Dispersion Science and Technology, 4 - (1), 29-45 (1983) a study of the precipitation of silver chloride in a micro-emulsion medium is presented. According to a particular embodiment described therein the ionic surfactant AEROSOL OT - (trade name of American Cyanamid Corp. for sodium (2-ethyl-hexyl) sulfosuccinate) was used in dry heptane to prepare a microemulsion of an aqueous silver nitrate solution and of an aqueous sodium chloride emulsion. For the precipitation of silver chloride, an aliquot of silver nitrate microemulsion was added to the same volume of a sodium chloride microemulsion and the mixture was rapidly shaken. A rapid exchange of reagents between the water pools (i.e. the aqueous salt phases) surrounded by the surfactant structure and the non polar heptane took place and the silver chloride was precipitated in the interior of inverted micelles also called reverse micelles.

The formation of inverted micelles in non-aqueous solvents is described e.g. by H.F. Eicke "Surfactants in non polar solvents -Aggregation and Micellation" Topics in Current Chemistry, Vol. 87 , p. 86-145 (1979), by A. Kitahora "Solubilization and Catalysis in Reversed Micelles", Advanced Colloid Interf. Science, 12, p. 109-140 (1980) and by L. Kagid "Solution Chemistry of Surfactants" K.L. Mittal - Ed. Plenum Press N.Y. Vol. 1, p. 427 (1979). A more recent study on inverted micelles can be found in the book "Reverse Micelles" edited by P. L. Luisi and B. E. Straub -Plenum Press -New York and London (1984).

The micelles of organic surfactant molecules in non polar solvents have the inverse structure of surfactant micelles in aqueous solutions. In aqueous surfactant solutions micelles have a hydrocarbon core, but in non polar organic solvents inverted micelles have a dense polar core containing water at the center of the micelle.

It is an object of the present invention to provide a process for the manufacture of a photothermographic material wherein use is made of the formation of minute amounts of photosensitive silver halide in tiny aqueous phase centers surrounded by a surfactant in an non polar liquid medium.

It is a further object of the present invention to provide a photothermographic material incorporating photosensitive silver halide in tiny aqueous phase centers surrounded by a surfactant in a solid non polar binder medium.

Other objects and advantages of the present invention will appear from the further description.

According to the present invention a process for the production of a photothermographic material is provided, which process comprises the steps of

1) producing inverted micelles having a polar core by mixing a surfactant in a non polar liquid medium in the presence of water being used in a minor amount with respect to the non polar liquid,

2) allowing to react in the water halide ions with silver ions so as to introduce in the polar core of said micelles minute amounts of silver halide,

3) forming a film forming photosensitive coating composition by mixing said micelles in said non polar liquid medium with a film forming polymeric organic binding agent that is soluble in said liquid medium, said liquid medium comprising a dissolved or dispersed developing agent for photo-exposed silver halide, and

4) coating said composition onto a support and allowing the non polar liquid to evaporate leaving a solid photosensitive layer on said support.

When speaking of "a minor amount of water with respect to the non polar liquid" in the present description and claims is meant less than 10 % by volume of water with regard to the volume of the non polar liquid.

According to an embodiment a hydrophilic colloid, e.g. gelatin, is introduced into the core of said micelles.

According to another embodiment said photosensitive layer is applied in association with a sub coat and/or top coat containing a developing agent capable of diffusing on heating into the photosensitive layer.

Surfactants are amphiphatic substances characterized by a relatively large non polar hydrophobic molecule part carrying chemically linked thereto a polar hydrophilic molecule part, whereby said substances have the property of lowering the surface tension of water.

Surfactants suited for use in the production of inverted micelles are either cationic, anionic or non-ionic surfactants.

In cationic surfactants the ion containing the organic part of the molecule is a cation. Examples of cationic surfactants are : alkylammonium salts and salts of higher molecular weight amines. In anionic surfactants the ion containing the organic part of the molecule is an anion. Examples of anionic surfactants are : higher carboxylic acid metal soaps, sulphosuccinates, higher alkyl sulphonates and alkylaryl sulphonates.

Examples of non-ionic surfactants are alkyl or alkylaryl substituted polyoxyalkylene compounds such as isooctylphenyl polyoxyethylene ethers.

Preferred surfactants for the formation of inverted micelles with relatively large capacity to include an aqueous liquid in their core are amphiphiles having two separate hydrocarbon chains or one branched hydrocarbon chain linked to the ionic structural part. Examples of such surfactants are : the sodium salts of C_6-C_{18} alkyl diesters of phosphoric acid, mono(2-hexyl-decyl) phosphoric acid ester and di-(2-ethylhexyl)-sulphosuccinic acid. Particularly suited for including a high amount of aqueous liquid are further amphiphiles having an ionic part of the betaine type as e.g. in amino-carboxylic acids such as $R\text{-}NH\text{-}(CH_2)_n\text{-}COOH$, wherein R is C_{12}-C_{18} alkyl and n is 1 to 4.

According to a first embodiment for the production of silver halide inside the core of inverted micelles a cationic surfactant having a halide counter ion is dispersed in the presence of a minute amount of water in an non polar solvent, e.g. an aliphatic, cycloaliphatic or aromatic hydrocarbon liquid or mixtures thereof, to form inverted micelles and a minor amount of water containing a dissolved silver salt, e.g. silver nitrate, is mixed therewith and at least partly introduced into the core of said micelles to obtain the formation of silver halide inside said core.

According to a second embodiment for the production of silver halide inside the core of inverted micelles an anionic surfactant having a silver counter ion is dispersed in the presence of a minute amount of water in a non polar solvent, e.g. an aliphatic, cycloaliphatic or aromatic hydrocarbon liquid or mixtures thereof, to form inverted micelles and a minor amount of water containing a dissolved

halide salt, e.g. sodium chloride, is mixed therewith and at least partly introduced into the core of said micelles to obtain the formation of silver halide inside said core.

According to a third embodiment for the production of silver halide inside the core of inverted micelles, inverted micelles are formed by dispersing a surfactant in the presence of a minor amount of water containing a water-soluble silver salt, e.g. silver nitrate, in a non polar solvent, and a minor amount of water containing a dissolved halide, e.g. ammonium bromide, is mixed therewith whereby at least a part of the aqueous solution of the halide salt becomes introduced into said cores and the formation of silver halide occurs inside said cores.

According to a fourth embodiment for the production of silver halide inside the core of inverted micelles, inverted micelles are formed by dispersing a surfactant in the presence of a minor amount of water containing a water-soluble halide salt, e.g. sodium chloride, in a non polar solvent, and a minor amount of water containing a dissolved silver salt, e.g. silver nitrate, is mixed therewith whereby the aqueous solution of the silver salt becomes at least partly introduced into said cores and the formation of silver halide occurs inside said cores.

According to a fifth embodiment for the production of silver halide inside the core of inverted micelles a first group of inverted micelles is formed by dispersing a surfactant in the presence of a minor amount of water containing a water-soluble silver salt, e.g. silver nitrate, in a non polar solvent, a second group of inverted micelles is formed by dispersing a surfactant in the presence of a minor amount of water containing a water-soluble halide salt, e.g. ammonium bromide, in said non polar solvent, and said both groups of micelles are mixed so that the aqueous contents of the cores become intermixed and the formation of silver halide occurs inside said cores.

According to a sixth embodiment for the production of silver halide inside the core of inverted micelles the inverted micelles are formed by mixing simultaneously in a non polar liquid medium in the presence of a minor amount of water a cationic surfactant having an halide, e.g. chloride, as counter anion and an anionic surfactant having a silver ion as counter cation.

Amounts of lightsensitive silver halide of 1 to 30 % with respect to the the non-lightsensitive silver salt will suffice to form catalytically active silver in the thermal reduction process.

Organic silver salts that are substantially insensitive to light and that are used in the present photothermographic material as substances yielding image-silver are preferably silver salt surfactants forming the inverted micelles having inside their cores photosensitive silver halide, but silver sulphonates with higher alkyl (C_{12}-C_{22}) groups and silver salts of aliphatic carboxylic acids known as fatty acids, so-called silver soaps that preferably contain at least 12 carbon atoms, for example silver behenate and silver stearate may be used in addition thereto although they have to be applied in dispersed form because these salts are inherently insoluble in non polar liquids such as n-heptane.

The use of silver dodecyl sulphonate in a photothermographic recording material is described e.g. in US-P 4,504,575.

As described e.g. in US-P 3,770,448 and US-P 4,435,499 silver behenate and silver stearate may be used in the presence of free fatty acid, e.g. behenic acid, which means that the recording composition of photothermographic materials need not to be alkaline to become developable. Other non-lightsensitive silver compounds for use in thermographic recording materials are described in GB-P 1,111,492.

The non-lightsensitive silver salts for use according to the present invention have preferably a relatively low melting point, preferably lower than 100°C, to become intimately mixed on heating with the silver nuclei that are formed by the reduction of the silver halide inside the inverted micelles. On heating the present photothermographic recording material the inverted micelles will desaggregate and catalytic contact of the photo-exposed silver halide with the non-photosenstive silver compound yielding the major part of the image silver will be made.

According to a preferred embodiment an anionic surfactant containing silver counter ions is used in such amounts that it does not only serves for yielding sufficient silver ions in the formation of minute amounts of photosensitive silver halide inside the cores of the inverted micelles but also provides the necessary quantity of silver ions for an image-forming thermal development following the image-wise exposure of the photothermographic material.

A particularly suitable anionic surfactant for that purpose is the silver salt of di-(2-ethylhexyl)-sulphosuccinic acid which forms inverted micelles in a non polar solvent such as n-pentane, n-hexane, n-heptane, n-octane, n-nonane, benzene, cyclohexane, carbon tetrachloride and 2,2-dimethylbutane. Other sulphonates that form inverted micelles in non polar solvents, e.g. in n-heptane, are tripentylmethylbenzene sulphonate and dinonylnaphthalene sulphonates. The latter forms smaller micelles in benzene than in n-decane.

The preparation of the silver salt of di-(2-ethylhexyl)-sulphosuccinic acid proceeded e.g. as follows :

13.3 g (30 mmole) of sodium di-(2-ethylhexyl)-sulphosuccinate were dissolved in 900 ml of dis-

tilled water by stirring vigorously. To the obtained solution a solution of 10.2 g (60 mmole) of silver nitrate in 20 ml of water were added while maintaining said stirring. The solution became slightly opalescent. Stirring was continued for 4 h at 20 °C. Thereupon the aqueous liquid was extracted with diethyl ether, once with 200 ml and thrice with 100 ml. After separation residual water was removed and the ether of the extract was evaporated under reduced pressure. The white solid residue was introduced into methanol in the presence of decolourizing carbon and stirred for 4 h at 20 °C. After filtration and evaporation of the methanol a white wax-like substance was obtained and dried for 12 h at 20 °C.

Yield : 12 g. The silver content defined by titration was 15.53 %, which corresponds with a conversion from sodium salt into silver salt of 77 %.

The preparation of silver di-(2-ethylhexyl)-sulphosuccinate may proceed likewise in an analogous way to the preparation of silver salts of fatty acids described in US-P 3,700,458.

Reducing agents acting as developing agents for photo-exposed silver halide in a thermographic recording material according to the present invention are e.g. hydroquinone and derivatives thereof which in order to counteract their oxidation by oxygen of the air are preferably used in an acidic medium. Preferred developing agents withstanding better aerial oxidation are o-alkyl-substituted phenols, aminophenols and methoxy-naphthol and derivatives thereof. Examples of suitable o-alkyl-substituted bisphenols as reducing agents for photothermographic recording materials are described in the published German Patent Application (DE-OS) 2,321,328 and US-P 3,679,414, 3,589,903 and 3,589,901. Still other reducing agents for use in photothermographic recording materials are described in Research Disclosure June 1978, item 17029.

Other ingredients that are useful in the image-formation on thermal processing are e.g. substances liberating alkali on heating, so-called alkali-precursors. Representatives thereof are described in the last mentioned Research Disclosure. Particularly useful for liberating alkali by thermal decarboxylation is guanidinium trichloroacetate. Other such precursors are, e.g. urea and the silylamines described in GB-P 1,141,591 yielding ammonia on heating above 80°C and/or co-crystal adducts of bisphenols and amines as described e.g. in US-P 3, 076,707 liberating an amine on heating.

Still other useful ingredients are image tone modifiers (toning agents) and chemical and spectral sensitizers.

The thermographic recording layer may in order to improve the photographic speed contain pigments that are n-type photoconductors. Such pigments are, e.g. titanium dioxide and photoconductive zinc oxide prepared by the reduction of zinc vapour (French process). The use of zinc oxide in thermographic recording materials is described e.g. in US-P 3,457,075.

In order to improve the total and/or spectral sensitivity of the photothermographic material prepared according to the present invention any suitable chemical and/ spectral sensitizing agent known in silver halide photography may be used, which agents in order to come into contact with the silver halide are incorporated into the aqueous medium in the core of the inverted micelles.

Toning agents that are preferably used in a thermographic recording material according to the present invention are phthalazinone derivatives as described e.g. in GB-P 1,420,815.

For the manufacture of the photothermographic recording materials according to the present invention the above inverted micelles are incorporated in an appropriate film forming binder that is soluble in the non polar solvent in which the formation of the micelles took place. Suitable film forming binding agents that are soluble in aliphatic or cycloaliphatic hydrocarbon liquids are e.g. : a copolymer of isobutylmethacrylate, stearylmethacrylate, methacrylic acid (75/24.8/0.2 % by weight), a copolymer of styrene and dodecyl methacrylate, a copolymer of isobutylmethacrylate, lauryl-methacrylate, methacrylic acid, and a copolymer of vinyltoluene, isobutylmethacrylate, stearyl-methacrylate (60/20/20 % by weight) and low molecular weight polybutene.

The support used in a photothermographic recording material according to the present invention may be a paper or resin film support, e.g. of the type described in Research Disclosure June 1978, item 17029.

While paper and film supports with glass transition temperature above 190°C are preferred other materials that can withstand processing temperatures, e.g. in the range of 80 to 150°C, may be used likewise, e.g. glass and metal supports.

The photothermographic recording layer may be coated with an overcoat layer to make it less susceptible to finger print marks and scratches that may occur in the heat processing. Suitable overcoat layers are described likewise in the already mentioned Research Disclosure wherein also a number of ingredients for colour developing photothermographic recording materials has been disclosed. Suitable ingredients for the production of

colour images are e.g. colour couplers that will react with oxidized reducing or developing agent or are leuco dyes that become imagewise oxidized on thermal processing.

The following examples illustrate the present invention without, however, limiting it thereto. All ratios and percentages are by weight unless otherwise indicated

EXAMPLE 1

For the manufacturing of a thermographic recording material according to the present invention the following compositions A, B, C, and D were prepared.

Composition A.

0.618 g (0.006 mole) of sodium bromide in 10 ml of distilled water.

Composition B.

5 g of copolymer of isobutylmethacrylate, stearylmethacrylate, methacrylic acid (75/24.8/0.2 %) dissolved in 50 ml of n-heptane by sonication (ultrasound treatment).

Composition C.

0.55 g (0.005 mole) of hydroquinone were dissolved in 10 ml of distilled water.

Composition D.

6.6 g of silver (di-2-ethylhexyl) sulphosuccinate - (prepared as described herein) were dissolved in 50 ml of composition B by sonication.

For preparing a photothermographic film 2.5 ml of composition D were added to a sufficient amount of composition B to obtain a total volume of 5 ml. Thereupon 50 microliter of composition C were added and mixed by sonication. After that mixing step 130 microliter of composition A were added and sonication was continued till the obtaining of a white turbid dispersion. The thus obtained mixture was coated onto a polyethylene terephthalate support at a wet coating thickness of 200 µm and dried at the atmosphere to remove the n-heptane.

The dried photothermographic layer had a total silver compound content corresponding with 0.88 g of silver per m2, and more particularly contained per m2 0.280 g of AgBr, 3 g of water and 8.3 g of the copolymer of composition C.

The dried film was exposed during 5 min through a half-tone pattern using 360 nm light of a UV lamp applied in chromatography, treated for 1 min with ammonia vapour and heated for 5 min at 100 °C.

The density (D) obtained in the exposed area was 0.8.

EXAMPLE 2

Example 1 was repeated with the difference however, that the hydroquinone was replaced by bis(4-hydroxyphenyl)-2,2′-propane (bisphenol A).

In a flask of 5 ml 138 microliter of distilled water and 2.5 ml of composition D of Example 1 were added to 110 mg of bisphenol A and mixed therewith by sonication. 150 microliter of acetone were added to obtain a clear liquid and thereupon composition B and 42 microliter of composition A of Example 1 were added while continuing the sonication to obtain a turbid dispersion.

The film material was prepared and exposed as described in Example 1.

The density (D) obtained in the exposed area was 0.510.

5.7 mg of the potassium salt of hydroquinone monosulphonic acid were added to 154 microliter of distilled water and thereupon 2.5 ml of composition D of Example 4. The mixture was sonicated till clear and composition B and 26 microliter of aqueous sodium bromide (prepared by dissolving 1.5 g of NaBr in 5 ml of distilled water) were added while continuing sonication. A white turbid mixture was obtained.

The thus obtained mixture was coated onto a polyethylene terephthalate support at a wet coating thickness of 200 um and dried at the atmosphere to remove the n-heptane.

The dried photothermographic layer contained per m2 0.280 g of AgBr, 3 g of water and 8.3 g of the copolymer of composition C.

The dried film was exposed as described in Example 1 and treated for 1 min with ammonia vapour and heated for 5 min at 100 °C.

The density (D) obtained in the exposed area was 2.5.

EXAMPLE 4

To 6.1 mg of the potassium salt of hydroquinone monosulphonic acid and 9.6 milligram of guanidininium trichloroacetate, 154 microliter of distilled water were added to obtain a solution. Thereto 2.5 ml of composition D of Example 1 were added and the mixture was sonicated till clear. To the obtained mixture a sufficient amount of composition B of Example 1 was added to obtain a final volume of 5 ml. Thereupon 26 microliter of an aqueous 3 molar sodium bromide solution was added and sonication was continued whereby a turbid dispersion was obtained.

The thus obtained dispersion was coated onto a polyethylene terephthalate support at a wet coating thickness of 200 µm and dried at the atmosphere to remove the n-heptane.

The dried film was exposed for 20 s through a half-tone pattern in a DUPLIPHOT HS 130 (trade name of Agfa-Gevaert N.V. Belgium for a contact-exposure apparatus) operating with eight 125 Watt mercury vapour lamps emitting UV-radiation. The density (D) built up in the exposed area was 0.98.

Claims

1. A process for the production of a photothermographic material comprising the steps :

1) producing inverted micelles having a polar core by mixing a surfactant in a non polar liquid medium in the presence of water being used in a minor amount with respect to the non polar liquid,

2) allowing to react in the water halide ions with silver ions so as to introduce in the polar core of said micelles minute amounts of silver halide,

3) forming a film forming photosensitive coating composition by mixing said micelles in said non polar liquid medium with a film forming polymeric organic binding agent that is soluble in said liquid medium, said liquid medium comprising a dissolved or dispersed developing agent for photo-exposed silver halide, and

4) coating said composition onto a support and allowing the non polar liquid to evaporate leaving a solid photosensitive layer on said support.

2. A process according to claim 1, wherein into the core of said micelles a hydrophilic colloid is introduced.

3. A process according to claim 1 or 2, wherein said photosensitive layer is applied in association with a sub coat and/or top coat containing a developing agent capable of diffusing on heating into the photosensitive layer.

4. A process according to claim 1, wherein for the production of silver halide inside the core of inverted micelles cationic surfactant having halide counter ions is dispersed in the presence of a minute amount of water in the non polar solvent to form inverted micelles and a minor amount of water containing a dissolved silver salt is mixed therewith and at least partly introduced into the core of said micelles to obtain the formation of silver halide inside said core.

5. A process according to claim 1, wherein for the production of silver halide inside the core of inverted micelles anionic surfactant having silver counter ions is dispersed in the presence of a minute amount of water in the non polar solvent to form inverted micelles and a minor amount of water containing a dissolved halide salt is mixed therewith and at least partly introduced into the core of said micelles to obtain the formation of silver halide inside said core.

6. A process according to any of claims 1 to 3, wherein for the production of silver halide inside the core of inverted micelles, inverted micelles are formed by dispersing a surfactant in the presence of a minor amount of water containing a water-soluble silver salt in the non polar solvent, and a minor amount of water containing a dissolved halide is mixed therewith whereby at least a part of the aqueous solution of the halide salt becomes introduced into said cores and the formation of silver halide occurs inside said cores.

7. A process according to any of claims 1 to 3, wherein for the production of silver halide inside the core of inverted micelles, inverted micelles are formed by dispersing a surfactant in the presence of a minor amount of water containing a water-soluble halide salt in the non polar solvent, and a minor amount of water containing a dissolved silver salt is mixed therewith whereby the aqueous solution of the silver salt becomes at least partly introduced into said cores and the formation of silver halide occurs inside said cores.

8. A process according to any of claims 1 to 3, wherein for the production of silver halide inside the core of inverted micelles, a first group of inverted micelles is formed by dispersing a surfactant in the presence of a minor amount of water containing a water-soluble silver salt in an non polar solvent, a second group of inverted micelles is formed by dispersing a surfactant in the presence of a minor amount of water containing a water-soluble halide salt in said non polar solvent, and said both groups of micelles are mixed so that the aqueous contents of the cores become intermixed and the formation of silver halide occurs inside said cores.

9. A process according to any of claims 1 to 3, wherein for the production of silver halide inside the core of inverted micelles inverted micelles are formed by mixing simultaneously in a non polar liquid medium in the presence of a minor amount of water a cationic surfactant having an halide ion as counter anion and an anionic surfactant having a silver ion as counter cation.

10. A process according to any of the claims 1 to 9, wherein in the preparation of the inverted micelles an anionic surfactant containing silver counter ions is used in such amounts that it does not only serves for yielding sufficient silver ions in the formation of minute amounts of photosensitive silver halide inside the cores of the inverted micelles but also provides the necessary quantity of silver ions for an image-forming thermal development following an image-wise photo-exposure of the photothermographic material.

11. A process according to claim 10, wherein as anionic surfactant the silver salt of di-(2-ethylhexyl)-sulphosuccinic acid is used.

12. A process according to any of the claims 1 to 11, wherein as developing agent for photo-exposed silver halide in said thermographic recording material hydroquinone or derivatives thereof or an o-alkyl-substituted phenol, aminophenol, methoxy-naphthol or derivative thereof is incorporated.

13. A process according to any of the claims 1 to 12, wherein in said thermographic recording material a substance yielding alkali on heating is incorporated.

14. A process according to any of the claims 1 to 13, wherein in said thermographic recording material titanium dioxide and/or photoconductive zinc oxide is (are) incorporated.

15. A thermographic recording process, wherein a thermographic recording material prepared according to any of the claims 1 to 14 is image-wise photo-exposed and overall heated to develop therein a visible image.

16. A photothermographic recording material comprising minute amounts of photosensitive silver halide in admixture with a substantially non-light-sensitive organic silver salt, wherein said material has been prepared according to a process of any of the claims 1 to 14.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 86 20 2055

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	US-A-3 457 075 (D.A. MORGAN) ---		G 03 C 1/02
D,A	FR-A-2 090 961 (AGFA-GEVAERT) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			G 03 C 1

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03-03-1987	PHILOSOPH L.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
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